

Space charge limited positive and negative photoconductivity in CdTe thin films

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Abstract : Thermally evaporated CdTe thin films having thickness in the range of 1000–4700 Å and deposited within the substrate temperature 473K–583K, show weak crystallinity and cause both space charge limited positive and negative photoconductivity. The occurrence of negative photoconductivity depends on the applied field, temperature and the illumination level, which is governed by the minority carrier holes optically freed from the trapping centers. The prime deep trap depths responsible for negative photoconductivity are 0.514 ± 0.002 eV and 0.516 ± 0.002 eV estimated from thermally stimulated current as well as SCLC measurements. The positions of electron Fermi level and recombination centers are calculated as 0.57 eV and 0.77 eV for *n*-type CdTe thin films.

Keywords : CdTe thin film, negative photoconductivity, annealing, defects, SCLC mechanism

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1. Introduction

Cadmium telluride is one of the most promising II-IV materials in recent years because of its wide range of applications in solar cell and other opto-electronic devices. A variety of works have already been done by various workers for structural, electrical and optical characterization of CdTe thin films during last two decades [1-10]. Some of the native and foreign imperfections centres also have been identified and confirmed from their influence on the measured properties. However, a further knowledge on defects is often desirable for better understanding of various physical processes like superlinearity, optical quenching, negative photoconductivity and other anomalous effects occurred in CdTe films [11,12]. From the technological point of view, it is also equally important to understand the origins and reduction of those defects in order to achieve better performance, yield and reliability of devices [13].

Defects usually creep into the films during preparation and subsequent exposure to atmosphere or gases. If the thicknesses of films are small, the surface states originated from the residual gases greatly influence the properties of films. In CdTe, it is suggested that the chemisorbed oxygen which even may form

CdO or TeO₂, should be taken into account for better dealing with the structure and photoelectronic properties of films [8,14]. The external light even promotes oxygen chemisorptions on *n*-type CdTe films resulting in a reduced conductivity [5,6]. Hence, the space charges originated from those surface states as well as the inherent native defects can play a key role in determination of film properties. In particular, space charge limited conduction can provide useful information on trap levels as suggested by other workers [3,4,15]. Negative photoconductivity is the consequence of presence of those multiply charged centres above the Fermi level [12]. Several workers have reported the occurrence of negative photoconductivity in II-IV class of films and other materials [16-18]. Stockmann had made a precise formulation of negative conductivity and in general, it is quite capable of explanation of most of such type phenomena [12]. Indeed from these studies, it is also realized that some light controlled detectors, switching devices might be fabricated by exploiting the results. In this paper, the predominance of surface states has been observed which leads to trap limited SCL (Space Charge Limited) negative conductivity in CdTe films. Using relevant SCLC (Space Charge Limited Conductivity) theory, some of basic transport parameters are calculated and correlated to the intensity of light.

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2. Experimental

Thin films of CdTe were deposited on clean glass substrates held at temperature 473K to 583K by usual thermal evaporation technique (HINDHIVAC 12A4) in a vacuum $\sim 10^{-5}$ torr. The source to substrate distance was kept at 3.2cm. and the deposition rate at 5 Å/s. A high purity (99.999%) bulk CdTe power obtained from Koch Light Lab., UK was used for deposition. Gap type geometry with a gap of 3mm between two pre-evaporated Al electrodes, was used for photoconductivity study. The thickness (t) of the film was measured using the multiple beam interferometry method with an accuracy of ± 20 Å. The ambient temperature as well as substrate temperature (T_s) was measured by putting a cu-cons thermocouple behind the substrate in conjunction with a digital microvoltmeter. The dark and photocurrent was measured with the help of high impedance ($\sim 10^{14}\Omega$) electrometer amplifier (ECIL 815) with an accuracy of $\pm 3\%$. A sensitive Aplan luxmeter was used for light intensity measurement. The film was kept inside a continuously evacuated glass tube during current measurement. All the measuring assembly was housed inside a properly grounded shielding network in the form of a floating Faraday cage to minimize the undesirable pick up noise.

3. Results and discussion

3.1. Structural effects :

The as-grown CdTe films deposited at $T_s \geq 473$ K were polycrystalline having *fcc* zincblende type structure. These films

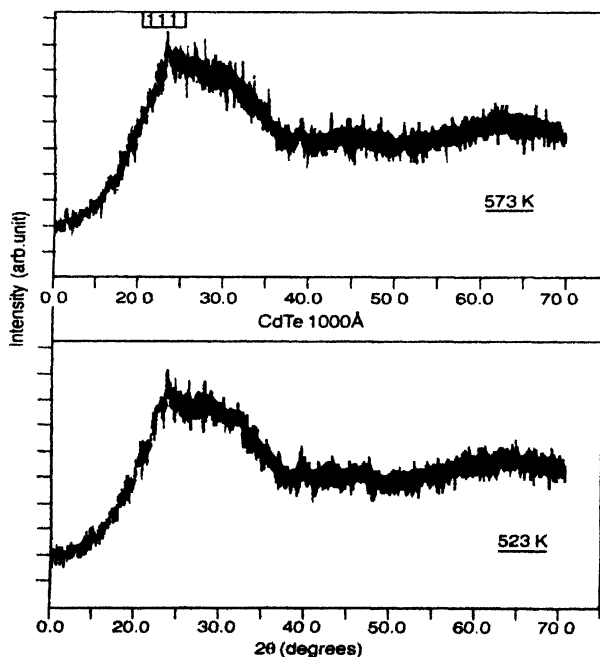


Figure 1. XRD traces of two CdTe films having thickness 1000Å and deposited at 523K and 573K.

show a sublinear behaviour of photocurrent-light intensity characteristics because of predominance of bimolecular recombination process and indirect transition at 1.7eV which have been reported in our earlier communications [19,20]. However, the CdTe films grown in the same T_s range show a weak diffraction line along [111] superimposed on a residual hump when the source to substrate distance is kept at 3.2 cm. XRD traces of two typical CdTe films deposited at 523K and 573K are shown in Figure 1. This clearly indicates the existence of amorphous phase along with the cubic zincblende type structure. The weak preferred orientation after an initial random orientation may occur in high melting point material like CdTe on chemisorbed of residual gases, during preparation [14]. Similar XRD traces are also found in ZnTe films. Amorphous phase certainly gives rise to a high defect density in these films. The film resistivities were in the range of $8.8 \times 10^6 - 1.0 \times 10^8 \Omega\text{m}$ and show poor photosensitivity. Poor sensitivity for low thickness films is due to the fast recombination of photo-excited minority carriers surface traps.

3.2. I (Current)- V (Voltage) characteristics :

The I - V characteristics of the CdTe films were examined in dark and under external illuminations as shown in Figure 2. It is observed that the conduction is ohmic at low field and is of trap limited space charge-limited type at high field as the slope increases and becomes greater than 2 [21]. The trap limit is

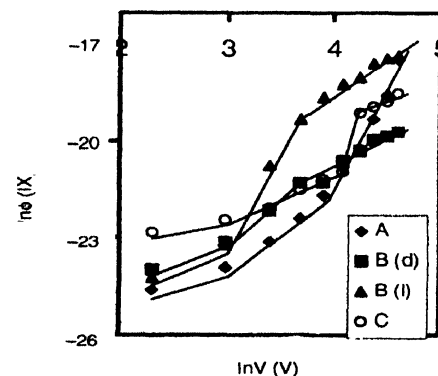


Figure 2. I - V characteristics of CdTe films. A: 1000Å(t), 473K(T_s). B (d): 2000Å(t), 473K(T_s) in dark; B (I): 2000Å(t), 473K(T_s) under illumination 8000lx; C: 4700Å(t), 573K(T_s).

obtained afterwards at sufficient high field. However, as-grown fresh CdTe film having thickness 3000Å deposited at 583K shows ohmic behaviour in dark. But the slope increases abruptly at low field region on increasing the intensity of light (Figure 3a). This in turn, causes a negative photoconductivity at low field and is described in Section 3.4. On annealing the film at 398K for 3hrs., the characteristics show the usual SCLC mechanism in dark and under illumination (Figure 3b).

3.3 SCLC mechanism :

The conduction mechanism in compound thin films is mainly governed by the grain boundary defect states [1,19,22-24]. The defect states depend on the film crystallinity. In the present work, as the crystallinity of films is poor due to the interaction of amorphous phase as revealed by XRD traces, the grain boundary states originated from dangling bonds as well as the

where d is the gap between the electrodes and μ_0 is the electron mobility. It is quite established that CdTe films possess n -type with high resistivity when those are deposited at $T_s \geq 400K$ [7]. Therefore, the holes are treated as minority carriers. At high field, the SCLC density is governed by the exponential trap distribution, preferably with deep traps given by [2-4,25],

$$J = 9/8 \mu_e \epsilon \epsilon_0 (V^2/d^3). \quad (2)$$

Here, $\mu_e = \mu_0 \theta$ is the effective electron mobility due to trapping; ϵ_0 and ϵ are the permittivity of free space and dielectric constant of film material, respectively. θ is the ratio between the free electron density n_0 in the conduction band to the total electron density ($n_0 + n_t$), n_t being the density of trapped electrons, which can be expressed as [25]

$$\theta = n_0 / (n_0 + n_t) = I_1 / I_2 = (N_t / N_i) \exp(-E_t/kT). \quad (3)$$

Experimentally, I_1 and I_2 are the currents at the beginning of the trap-limited square law region to the end of the rise upto trap-filled limit V_{tfl} . E_t is the trap depth measured from the bottom of the conduction band, N_t being the effective density of states in the conduction band. The total density of traps N_t can be estimated from the relation

$$N_t = 2\epsilon\epsilon_0 / ed^2 V_{tfl}. \quad (4)$$

The equilibrium free electron density n_0 in the conduction band is calculated using the relation

$$n_0 = (\epsilon\epsilon_0 \theta / ed^2) V_t. \quad (5)$$

Hence, the transport parameters are calculated using above relations and represented in Table 1. The values agree well with the results of other workers [2,4,14] measuring similar SCLC current in thermally evaporated CdTe thin films. It is observed that the transition voltage V_t might depend on the film growth conditions as well as on the intensity of light. The intensity of light along with the ambient temperature can change the nature of the imperfection levels. At a sufficient high intensity of light, the trap-filled limit increases because of trapping effect. The measured trap depths 0.52eV to 0.586eV in the present study, may be attributed to the doubly-ionized Cd vacancies as well as chemisorbed oxygen [5,6,8]. In fact, under the action of light, those surface states might play the key role over other defects.

3.4. Negative photoconductivity :

When the dark current decreases on absorption of external radiations, it is defined as the negative photoconductivity. The photocurrent in the present work is expressed as

$$I_{ph} = I_l - I_d, \quad (6)$$

where I_l and I_d are the currents under illumination and in dark, respectively. Positive photoconductivity results for $I_l > I_d$ and

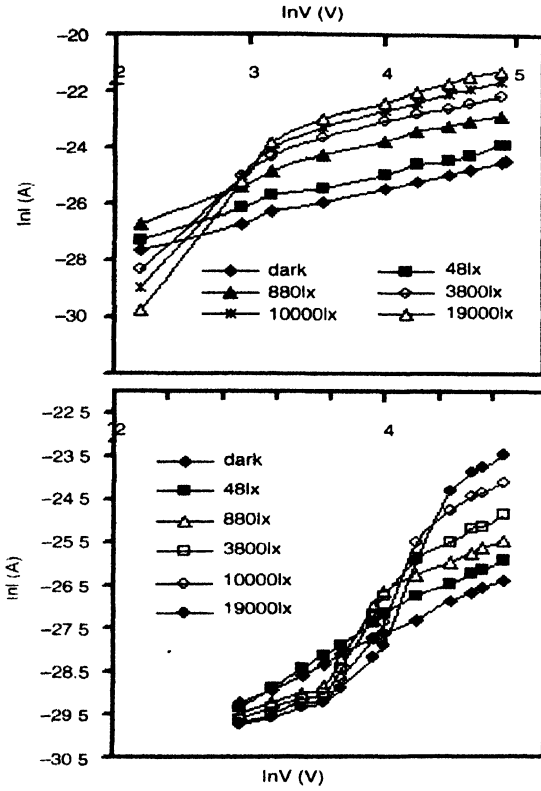


Figure 3. I - V curves for (a) fresh and (b) annealed CdTe film (3000Å) deposited at 583K.

chemisorbed oxygen and other impurities from atmosphere, may influence dark and photoconductivity. These localized states act as carriers trapping centers and after trapping the injected charges from the electrodes, they become charged and thereby build up space charges. The concentration of space charges is modified by the photo generated electron-hole pairs and causes positive or negative space charge limited current depending on the degree of ionization and their existence below or above the Fermi level.

At low bias upto transition voltage V_t at which the conduction changes from ohmic to SCLC, the current density J is governed by the intrinsic free carrier density n_0 given by [3,25],

$$J = n_0 \mu_0 V_t / d, \quad (1)$$

Table 1 Transport parameters viz: conductivity (σ), ratio of free electron density to total electron density (q), free electron density (n_f), trapped electron density (n_t), free electron mobility (μ_0), effective mobility (μ_e) and trap depths (E_t) estimated from SCLC measurements in CdTe thin films.

$n(\text{\AA})$ and T	White light (lx)	$\sigma(\Omega^{-1}m^{-1})$ $\times 10^{-8}$	q	$n_f(m^{-1})$ $\times 10^{14}$	$n_t(m^{-1})$ $\times 10^{14}$	$\mu_0(m^2V^{-1}s^{-1})$ $\times 10^{-4}$	$\mu_e(m^2V^{-1}s^{-1})$ $\times 10^{-4}$	$E_t(eV)$
3000 583K	Dark	2.63	0.166	1.5	0.759	1.095	1.80	0.520
	48	2.38	0.112	1.02	0.808	1.446	1.62	0.530
	880	2.16	0.110	1.84	1.49	0.729	0.801	0.530
	3800	1.80	0.104	1.74	1.51	0.646	0.673	0.532
	10,000	1.43	0.0242	0.406	1.63	2.2	0.532	0.562
	19,000	1.43	0.0071	0.119	1.65	7.5	0.532	0.586
2000 473K	dark	1.12	0.118	1.13	0.837	0.625	0.737	0.536
	8000	1.00	0.0200	0.192	0.938	3.28	0.656	0.581
4700 573K	dark	2.24	0.0358	0.343	0.923	4.09	0.146	0.552

that of negative photoconductivity for $I_f < I_d$. The films having thickness $< 3000\text{\AA}$ show poor photosensitivity with slow photocurrent rise and decay nature. However, a typical CdTe film deposited at 583K having thickness 3000\AA , shows both positive and negative photoconductivity corresponding to appropriate applied field, ambient temperature and intensity of light as shown in Figures 4(a--d). It shows superlinearity for low-level $\geq 48\text{lx}$ and afterwards, the photocurrent possesses maximum and then falls with further increase of light intensity (Figure 4a). Superlinearity clearly confirms the existence of class II type doubly- ionized defect states [11]. The reduction of photocurrent at high intensity light level gradually diminished with the increasing of applied field. At sufficient high field ($\sim 3 \times 10^4\text{ V/m}$), the characteristics show a sublinear relationship having slope 0.5. After thermal annealing, the film at 398K for 3 hrs, it is observed that the dark as well as photocurrent decrease sharply. The annealed film also shows the similar effect as in fresh (Figure 4b). The photocurrent becomes zero at some sufficient intensity of light and then increases (negative photocurrent) in reverse order with further increasing of light intensity. The negative photocurrent-light intensity curves (Figure 4d) shows that negative photocurrent increases rapidly at first and then attain a steady increasing trend with a nearly equal slope ~ 0.15 . At low applied field $6.3 \times 10^3\text{ V/m}$ and within the measuring ambient temperature range of 353K–393K, the photocurrent first decreases at a slower rate with increasing light intensity and then sharply falls (Figure 4c). This leads to negative photoconductivity for further increase of light intensity. The overall onset of negative photoconductivity ($I_{ph} = 0$) with respect to applied field and ambient temperature, is depicted in Figure 5. It is seen from the curves that the onset of negative photoconductivity increases with applied field and temperature *i.e* higher the field or temperature, higher the light intensity to be applied to initiate negative photoconductivity.

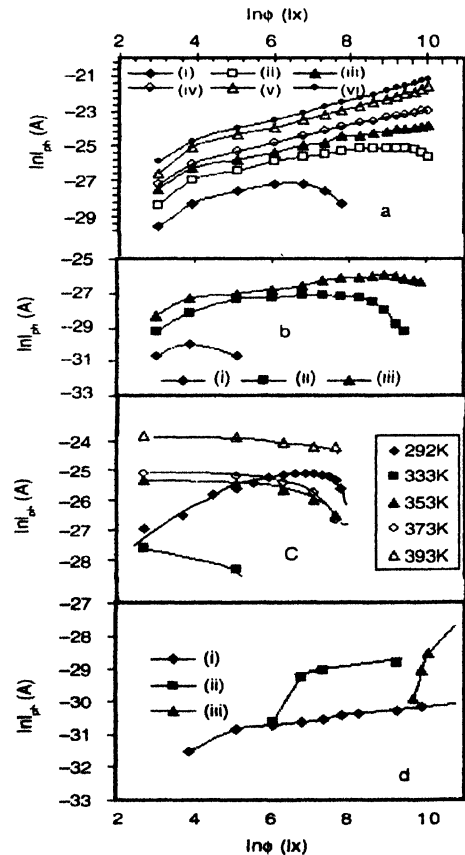


Figure 4. $\ln I_{ph}$ - $\ln \phi$ characteristics of (a) fresh CdTe film (3000\AA) deposited at 583K and measured at (i) $3 \times 10^3\text{ V/m}$, (ii) $6.3 \times 10^3\text{ V/m}$, (iii) $9.3 \times 10^3\text{ V/m}$, (iv) $11.6 \times 10^3\text{ V/m}$, (v) $3 \times 10^4\text{ V/m}$, (vi) $4.46 \times 10^4\text{ V/m}$; (b) after annealing and measured at (i) $1.2 \times 10^4\text{ V/m}$, (ii) $1.76 \times 10^4\text{ V/m}$, (iii) $2.4 \times 10^4\text{ V/m}$; (c) measured at different ambient temperatures and (d) Negative photocurrent—light intensity characteristics measured at (i) $6.3 \times 10^3\text{ V/m}$, (ii) $1.2 \times 10^4\text{ V/m}$, (iv) $1.76 \times 10^4\text{ V/m}$.

The observation reveals that the recombination kinetics is dominated by the class II states in correlation with the applied field and light level. According to Stockmann model, these states (level II) exist above the electron Fermi level and have a low

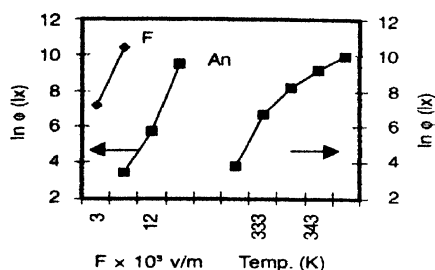


Figure 5 Onset of negative photoconductivity ($I_{ph}=0$) in fresh (F) and annealed (An) film corresponding to rise of ambient temperature.

thermal exchange with the conduction band at room temperature (Figure 6). When occupied, those are assumed to be the doubly-charged negative centers, preferably Cd vacancies and hemisorbed oxygen. The crosssection of level II for majority carrier electrons is less than the crosssection of level I of recombination centers. At low light intensity <48lx, level II enhance the electron free life time and thereby a superlinearity. But for subsequent higher intensity of light, the minority carrier holes are optically freed from those localized trapping centers. The free holes rapidly captured by the level I where they recombine with the majority carrier electrons from conduction band. This reduces the conductivity and thereby results negative photoconductivity. The increase of transit time of electron at high field then increases the free electron density at conduction band. Thus, a high applied field can promote conductivity with molecular recombination of carriers.

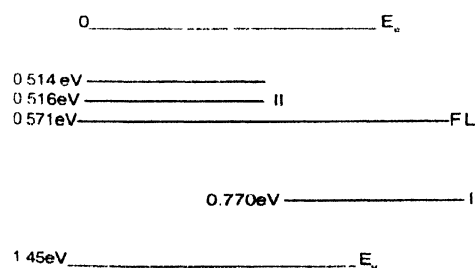


Figure 6. Energy level diagram (not in scale): I: Recombination level, II: trapping levels, FL: Fermi level, E_c : Bottom of conduction band, and E_v : Top of the valence band.

3.5. Temperature dependence of negative photoconductivity :

On rise of temperature increases the rate of ionization of level II. It is observed that the photocurrent sharply falls around 321K, which may be due to the maximum capture of photoelectrons at those ionized centers II. The photosensitivity (I_{ph}/I_d) which shows exponential dependence of temperature (Figure 7), clearly

reveals the occurrence of negative photoconductivity ($S<0$) in the range of 308-348K. Hence, the film conductivity changes from *n*-type to *p*-type for increasing temperature beyond 308K. Similar behaviour is also found by Uri [5] in neutron irradiated CdTe films. At high temperature > 348K, and at high light level ≤ 3800 lx, the effective number of photo-generated electrons reaching the conduction band via level II, is comparable to the electron lost due to recombination at level I. Hence photocurrent almost constant upto light level 3800lx (Figure 4c). At sufficient high light level > 3800lx, the recombination process predominate cause of more number of holes optically freed from the level I. The negative photocurrent initially rises sharply because of rapid recombination of free electron with the optically freed holes at level I. However, most of the centers at level II are optically freed at a sufficient light level corresponding to applied field and temperature, so that the recombination process attains a steady state. This causes a steady slow rise of negative photocurrent for further increase of light intensity (Figure 4d). The position of electron Fermi level and recombination level are estimated as 0.571 eV and 0.77 eV, in dark. The location of level II is calculated from TSC (Thermally Stimulated Current) measurement.

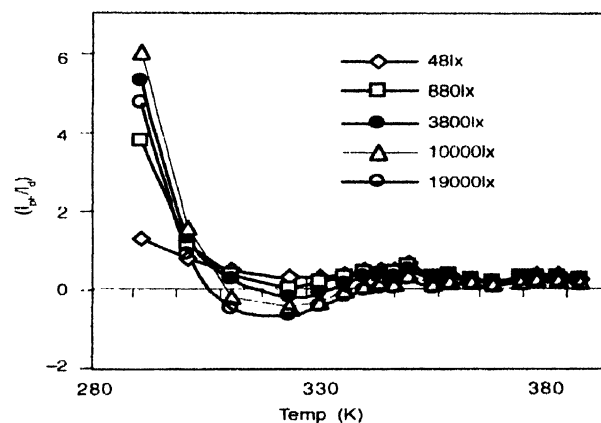


Figure 7. Temperature dependence of photosensitivity (I_{ph}/I_d).

3.6. Thermally stimulated current :

The temperature dependence of dark conductivity on heating and cooling in the range of 292K to 393K, is shown in Figure 8a. It shows thermally stimulated conductivity in the range of 315K to 326K which then increases linearly for further increase of temperature upto 393K. This indicates an extrinsic conduction upto 328K and afterwards, a band-to-band intrinsic process. On cooling cycle, the conductivity follows almost the same path, but falls sharply from 326 to 292K. The activation energies correspond to intrinsic range is 0.732 eV and 0.710 eV for heating and cooling cycles respectively. It is quite apparent that TSC curve exhibits two prominent maxima along with other two small shoulders (Figure 8b). Variation in the shape of TSC curve is a

direct result of variation of free carrier lifetime. Assuming the traps emptied with fast retrapping, the peak current occurs when the quasi- Fermi level crosses the trap level. According to Bube[12] the trap depth can be estimated from the relation

$$E_t = kT_m \ln[N_c e \mu / \sigma_m], \quad (7)$$

where σ_m is the maximum conductivity corresponding to temperature T_m . The density of states N_c is calculated for T_m . The electron mobility in the present work in dark, is found to be $10.95 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ that agrees well with the values reported by other workers [8]. Hence, this value is used for calculation of trap depth, which yields $0.514 \pm 0.002 \text{ eV}$ and $0.516 \pm 0.002 \text{ eV}$ corresponding to 315K and 321K of TSC maxima. These trap depths are also nearly supported by SCLC measurement in dark. As the TSC peaks are observed at higher temperature $> 300\text{K}$, these trap levels may be mainly due to surface traps of chemisorbed oxygen apart from the Cd vacancies. These chemisorbed oxygen atoms form doubly- ionized acceptor level II above Fermi level and makes a prime contribution to negative photoconductivity. It is also expected that annealing at 398K for 3 hrs. is not enough to remove those surface traps. Because after annealing the film rather shows a sharp increase of resistivity along with the pronounced effect of negative photoconductivity.

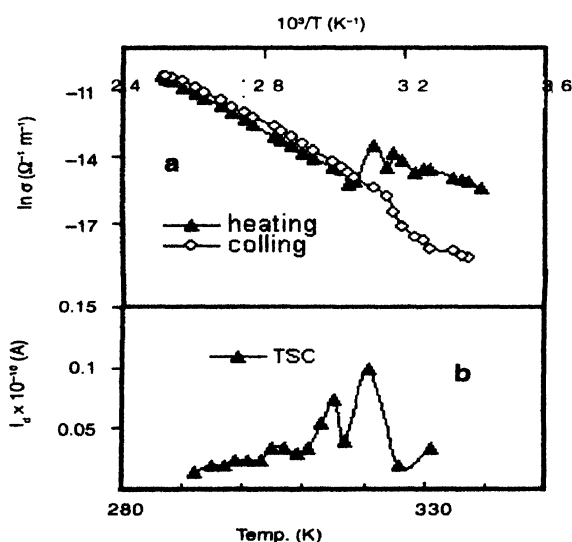


Figure 8. (a) Temperature dependence of dark conductivity on a heating and cooling cycle and (b) Thermally stimulated current (TSC) measurement during heating.

4. Conclusions

The CdTe films grown at high Ts in the range of 473K to 583K show a weak diffraction line along [111] direction with a superimposed residual hump. This clearly reveals the predominance of amorphous phase over the cubic crystalline structure. The I-V characteristics in dark and under illumination

show SCLC process governed by native Cd vacancies as well as surface traps owing to chemisorbed oxygen. The transport parameters along with the corresponding trap depths are calculated which are in conformity with the other reported results. The occurrence of negative photoconductivity is due to those doubly- ionized acceptor levels appearing above the Fermi level. The onset of negative photoconductivity depends on the applied field and temperature in co-relation with the illumination level. Negative photoconductivity increases rapidly at first and then attains a steady state for appropriate applied field and intensity of illumination. A TSC spectrum shows two prominent deep trap levels at $0.514 \pm 0.002 \text{ eV}$ and $0.516 \pm 0.002 \text{ eV}$, which are also in agreement with the SCLC measurement. The levels are quite responsible for occurrence of negative photoconductivity.

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